

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT

NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

ANNUAL REPORT

March 15, 1969 to September 14, 1969

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Report Prepared by

A. L. Ducoffe, Chairman

Georgia Tech Space Sciences Technology Board

October 15, 1969



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GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

Office of
The Vice President for
Academic Affairs

October 15, 1969

Dr. Francis B. Smith
Assistant Administrator for
University Affairs
National Aeronautics and Space
Administration
Washington, D. C. 20546

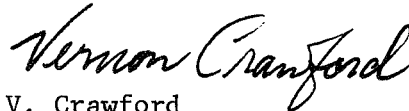
SUBJECT: Annual Report
March 15, 1969 to September 14, 1969
Multidisciplinary Research Grant NGL 11-002-018

Dear Dr. Smith:

The Georgia Institute of Technology Space Sciences and
Technology Board is pleased to submit herewith thirty (30) copies of
an annual report for Multidisciplinary Research Grant NGL 11-002-018.

We shall be pleased to provide any additional information
that you find necessary.

Sincerely yours,



V. Crawford
Vice President for
Academic Affairs

VC/rs

Enclosures

cc: Mr. H. L. Baker
Members of the Space Sciences and Technology Board

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ANNUAL REPORT

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

I. SUMMARY

The National Aeronautics and Space Administration granted the Georgia Institute of Technology \$600,000 on June 15, 1964, \$300,000 on June 15, 1965, \$300,000 on March 15, 1966, \$300,000 on March 15, 1967, and \$100,000 on March 15, 1968 for the support over six years and nine months of basic scientific research entitled "Multidisciplinary Research in the Space Sciences and Technology."

The grant funds have been used for the first five periods to support an expansion of multidisciplinary research programs in materials and materials processing, transport phenomena, energy conversion, systems, and nuclear processes.

The grant has been administered by the Space Sciences and Technology Board established at the Georgia Institute of Technology. The Chairman of the Board is Dr. A. L. Ducoffe, Director of the School of Aerospace Engineering. The other Board members are H. F. Bauer, Engineering Mechanics; C. H. Braden, Physics; W. O. Carlson, Acting Dean of Engineering; J. W. Hooper, Electrical Engineering; R. H. Kasriel, Mathematics; P. Kelly, Social Sciences; H. A. McGee, Jr., Chemical Engineering; and W. M. Spicer, Director, School of Chemistry.

The sixth grant period runs from March 15, 1969 through March 14, 1970. The present document reports the research results obtained during the first six months of this period.

An indication of the research activity stimulated by the grant during this reporting period is the publication in recognized journals of 3 papers and the submission of 8 additional. One paper has been read at a scientific meeting. During the present grant period 2 Undergraduate students, 5 Masters students, 18 Ph.D. students and 2 Post Doctorals participated in the research effort.

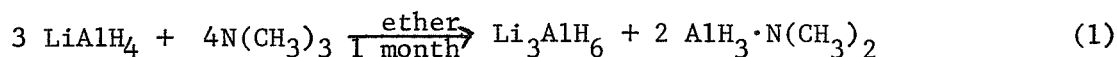
II. RESEARCH RESULTS

1. Complex Metal Hydrides. High Isp Fuel

Components - E. C. Ashby

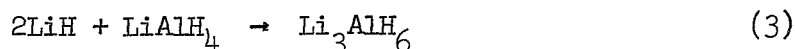
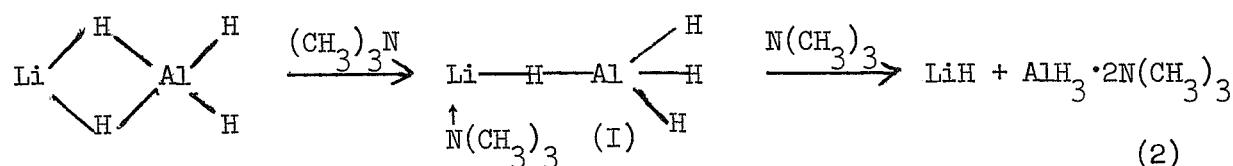
The program designed to elucidate the composition of complex metal hydrides in solution which was undertaken in October 1968 has been completed. A number of key factors in the extraction of MH_3 from compounds of the type $M'(MH_4)_n$ ($M'=Li, Na, (C_8H_{17})C_3H_7N$ and Mg ; $M = B, Al$) have been uncovered and much information has been gained about the mechanism of this reaction.

The interaction of $LiAlH_4$ and trimethylamine has been shown to give 100% yield of bis(trimethylamine)alane and Li_3AlH_6 .



This reaction proceeds through the solvate $LiAlH_4 \cdot N(CH_3)_3$. The

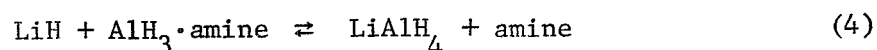
evidence for this intermediate is the LiAlH_4 and trimethylamine do not react in strongly basic solvents such as tetrahydrofuran (THF). In nondonor solvents such as benzene, the alane extraction process is far more rapid (complete in 3 days) than in the modestly basic solvent, ether. The same effect is noted with $\text{ClMg}(\text{AlH}_4)$ which undergoes alane extraction more readily when it is desolvated than as a tetrahydrofuran solvate. This leads to the proposed mechanism shown below.



A number of important points have been established concerning this mechanism. It was previously suggested that the complex (I) involved aluminum coordination by the amine. On the basis of a comparison of the infrared spectra of amine solvates (triethylenediamine (TEDA), trimethylamine, $\text{N,N',N'',N'''}\text{-tetramethylethylenediamine}$ (TMED), and triethylamine) of LiAlH_4 and NaAlH_4 with the corresponding amine alane, a model has been developed for predicting the trend in frequencies of aluminum-hydrogen vibrations which depend not only on the coordination number of the aluminum atom, but the degree of covalent interaction of the AlH_4 species with its counter ion. The second

important feature of the scheme proposed above is the removal of LiH from the system as insoluble Li_3AlH_6 .

The reaction shown below is a general reaction if certain conditions are met.



Either the solvent must be sufficiently basic that the amine generated by the reaction does not form a solvate with LiAlH_4 or the amine must be removed as it is formed. In the case of the reaction of bis(trimethylamine)alane with LiH in ether, a quantitative yield of LiAlH_4 can be obtained if refluxing ether is used and the liberated amine removed as it is generated. On the other hand, if the amine is not removed and the reaction is performed at room temperature, the alane extraction reaction dominates and the ultimate products are Li_3AlH_6 and bis(trimethylamine)alane.

The failure of LiBH_4 to undergo a borane extraction reaction can be explained by the inability of LiH generated by such a reaction to be removed from the reaction mixture as Li_3BH_6 which will not react with the amine borane. Complexes of LiBH_4 with TEDA, trimethylamine and triethylamine have been prepared and characterized. Trimethylamine does not interact with THF solvates of $\text{Mg}(\text{BH}_4)_2$ or ClMgBH_4 . Attempts to desolvate these compounds leads to borane extraction by THF.

A manuscript entitled "Composition of Complex Metal Hydrides in Solution. I. Tertiary Amines," has been recently submitted

to "Inorganic Chemistry." The experimental work reported herein was carried out by Dr. Joseph Dilts, a postdoctoral research assistant.

2. The Growth of Oxide-Metal Composites -

A. T. Chapman

In previous reports a description of the melting of refractory oxides using high frequency induction heating was described. This technique has been employed to grow non-metallic single crystals using an internal zone-melting scheme and, currently, to achieve unidirectional solidification needed for the growth of ordered composite structures in eutectic systems. The systems of interest are oxide-metal combinations.

Numerous lime (CaO) stabilized zirconia (ZrO_2) - 5 to 20 weight percent tungsten (W) mixtures in the form of pellets have been internally melted in a nitrogen atmosphere using a 13.7 MHz, 10 KW, RF generator. Microstructural examination revealed three distinctly different regions. Undoubtedly the most interesting region is shown in Figure 1 where W fibers were formed in the ZrO_2 matrix. The fibers can be seen extending below the surface into the matrix adjacent to cracks in the sample which provided more light for deeper viewing.

Coupled eutectic growth has previously been achieved in the system UO_2 -W and duplicating this solidification behavior in an additional refractory oxide-metal system suggests that a totally new combination of very high temperature materials are candidates for eutectic growth. (The wide differences in properties of the oxides and metals will produce materials of novel properties). The current

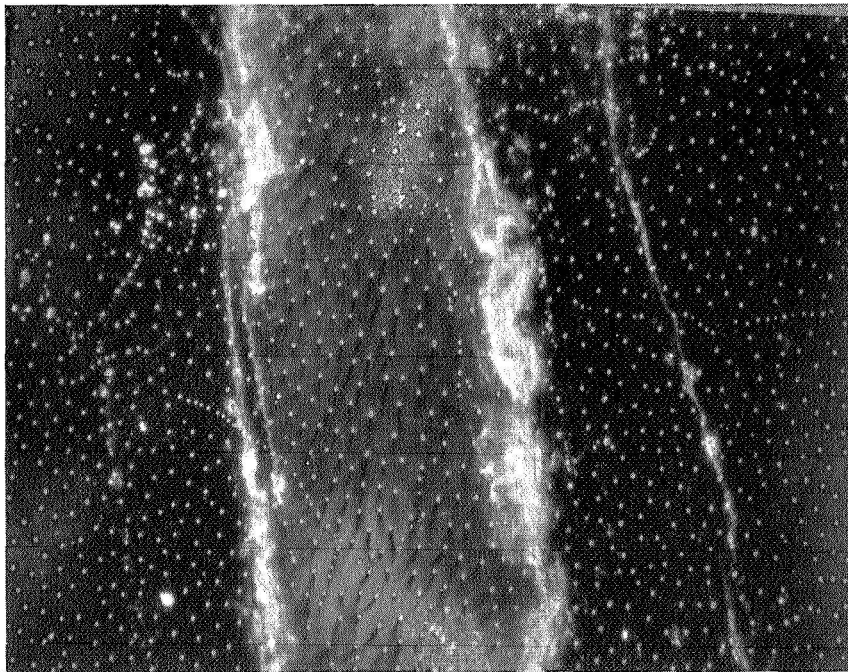


Figure 1. Tungsten fiber growth in a
CaO stabilized ZrO_2 matrix.
Dark Field 600X.

criteria for coupled growth in eutectic systems has been generated from data obtained primarily in metallic systems (and some organic studies). The ability to achieve eutectic growth in oxide-metal combinations violates some of these criteria and, perhaps, the initial significance of this study is the opportunity to broaden and reevaluate the parameters which control coupled growth in all types of systems.

The two additional regions found during the solidification of CaO stabilized ZrO_2 -W mixtures consisted of (1) a circumferential shell of essentially pure transparent ZrO_2 crystals and (2) an extensive internal region containing predominantly dendrites of ZrO_2 and voids partially filled with minor amounts of calcium tungstate (CaWO_3) and W. Figure 2 is typical of the dendritic region. Analysis of the parameters controlling the formation of these two regions along with the ordered fiber area is in progress.

During this report period three papers have been submitted for publication. The papers, " UO_2 -W Cermets Produced by Unidirectional Solidification" and "Solidification Behavior in the System CaO Stabilized ZrO_2 -W" were submitted to the Journal of the American Ceramic Society. A note entitled, "Refractory Oxide-Metal Composites: Scanning Electron Microscopy and X-ray Diffraction of UO_2 -W" was sent to Science.

Two M. S. students, David N. Hill and Christopher Yao are working on this project. In addition, Michael D. Watson completed an undergraduate thesis entitled, " ZrO_2 -W Cermets Produced by Unidirectional Solidification."

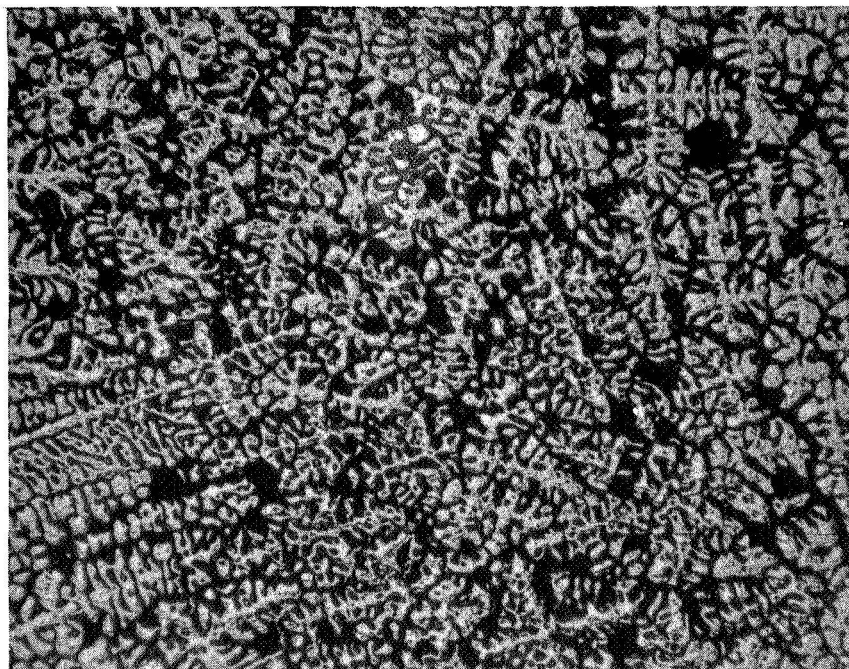


Figure 2. Solidification region of
CaO stabilized ZrO_2 -W
displaying ZrO_2 dendrites
and voids (dark areas).
Bright field 60X.

3. Nuclear Astrophysics - R. W. Fink

The only additional comments to be made since the semi-annual report of March 17, 1969, are as follows:

Funds for this project expired on June 30, 1969, and had been used entirely for the salary of Dr. N. RanaKumar, full-time postdoctoral research associate (terminated July 31, 1969).

Results described in the semiannual report of March 17, 1969, have now been published. Additional results have been obtained and submitted for publication in the following two papers:

W. Lu, N. RanaKumar, and R. W. Fink, "Activation Cross Sections for $(n, 2n)$ Reactions at 14.4 MeV in the Region of $Z = 40 - 60$: Precision Measurements and Systematics," Physical Review (submitted 1969).

W. Lu, N. RanaKumar, and R. W. Fink, "Activation Cross Sections for $(n,p)[(n,np) + (n,pn) + (n,d)]$, and (n, α) Reactions in the Region of $Z = 40 - 58$ at 14.4 MeV," Physical Review (submitted 1969).
Papers presented at meetings: The paper on $(n,2n)$ reactions listed above was presented by Dr. N. RanaKumar at the American Physical Society meeting, Washington, D.C., April, 1969, and an abstract appeared in Bull. Am. Phys. Soc. 14, No. 4, 495 (1969).

4. A Study of Helicopter Blade Slap Noise - R. B. Gray

The equipment for the experimental phase of the research has been retrieved from storage and is being set up in the laboratory. Plans for the experimental program are underway. Since the grant period has been increased from one to two years, the program will be

extended to cover this period of time.

5. Vibration and Stability of Distensible Fluid Lines

Carrying a Pulsating Incompressible Liquid -

J. Siekmann

Objectives of the Research:

Utilization of Fluid Transmission Lines in automatic control, liquid-propellant rocket and other systems requires knowledge of their dynamic response. In this study the symmetric and asymmetric modes of propagation for a viscous liquid in a cylindrical elastic conduit will be investigated.

Description of the Work Performed:

In order to understand the phenomenon of wave propagation in a fluid-elastic system with Poiseuille flow as basic flow, a perturbation method is employed. The equations of motion for the fluid (Navier-Stokes equations) as well as for the elastic conduit are considered. The mathematical problem is to find a solution for the perturbed velocity which satisfies the appropriate kinematic and dynamic conditions of coupled motion of the system.

Results:

Basic equations for the coupled motion for Poiseuille flow in an elastic conduit have been derived. The problem of wave propagation and stability of the fluid-elastic system has been studied. Mathematical solutions for some special cases such as vanishing mean flow velocity and frictionless cases have been found. For more general cases, a numerical treatment is employed. Some dynamic pro-

blems of fluid-elastic system are also being investigated. It is hoped that this will give some analogue and qualitative understanding of the problem, which is our main interest, but which is more difficult to solve.

Graduate Students Supported by this Project:

Mr. Shih-Chih Chang, Ph.D. student.

6. Atomic and Magnetic Ordering in Transition

Metal Alloys - S. Spooner

Objectives:

This multidisciplinary program has as its objective to understand the relationship between ordering phenomena and the physical properties of technically significant magnetic alloy systems. By coordinating solid state physics and metallurgical studies of selected alloys, a fundamental understanding motivated by practical objectives is sought. The work is centered on experimental studies using Mössbauer spectroscopy and neutron diffraction while theoretical studies of the statistical mechanics of ordering is carried on in parallel. The particular alloy system of iron-cobalt has been selected for its intrinsic scientific as well as practical interest. Study of nickel-manganese alloys with Dr. Starke in the School of Chemical Engineering is continuing as an extension of the interest in transition metal alloy system. We have had the opportunity to provide partial support for the studies of magnetic ordering in FeCO_3 . These studies have been a subject of common interest for the principal investigators relating to Ising model behavior which has been applied frequently to

alloy ordering behavior.

Description of Work:

Mössbauer spectroscopy studies of iron-cobalt are now completed and are reported in the thesis just finished by Benjamin DeMayo. Extension of these investigations to several other alloy compositions have added to an understanding of order-dependent features of the effective field at the nucleus. The great precision of this study exceeds any previous study and should provide valuable clues to the further development of a theoretical picture of the alloy behavior. The direction for a number of new experiments has been indicated, one of which is discussed below.

Among the new experimental directions suggested by Mössbauer investigations, one of the most intriguing is the investigation of the atomic moments in the iron-cobalt (50%) as a function of order using polarized neutron diffraction. Since there is no possibility of obtaining a single crystal of this alloy and a very high degree of precision is needed to measure the moments, plans have been made to carry out polarized neutron diffraction measurements at the Oak Ridge High Flux Isotope Reactor in cooperation with J. W. Cable. In this way polycrystalline samples can be investigated with the high flux polarized beam. Three alloy sets consisting of an ordered and a disordered alloy plate have been prepared. An initial measurement of neutron beam depolarization in the first alloy set has been made. Sample improvements have subsequently been made and further attempts at the experiments will be undertaken soon. The

degree of long-range order has been confirmed at the Georgia Tech reactor.

Studies of magnetic ordering in FeCO_3 (siderite) Mössbauer spectroscopy were supported during the recent summer months.

The work constituted the Ph.D. thesis of Norman Koon. The intrinsic interest in this system is the fact of its close resemblance to an ideal Ising model. Atomic moment relaxation times and sublattice magnetization were studied as a function of temperature and magnetic field. Of particular interest to our project was the examination of temperature-dependence of magnetic sublattice order. These studies gave a very precise determination of the critical exponent describing the temperature dependence.

Metallurgical aspects of alloy behavior are under continual study in connection with specimen preparation. The remarkable destruction of long-range order through deformation has been confirmed by further diffuse scattering studies. An upper bound for the first-neighbor short-ranged order coefficient has been established at 0.4 for powders produced by grinding. Annealing of these deformed powders produces long-ranged order rapidly at 500°C . Undeformed samples require longer time to produce the equivalent degree of order. The inter-relationship of the lattice defects, alloy order-domains and thermal history will receive further attention.

Theoretical studies of thermal behavior for a Heisenberg paramagnet have been done by Sam A. Scales as a Ph.D. thesis. Here double time, temperature dependent Green's functions are used to analyze the spin correlation functions. These theoretical predictions

should be useful for comparison with experimental studies of magnetic diffuse scattering in the paramagnetic region.

A study of spin correlations in the Heisenberg linear chain at infinite temperatures has been made and results compared with exact computer results.

Conclusions:

The conclusions derived from Mössbauer spectroscopy are quoted from Benjamin DeMayo's thesis: "Mössbauer spectroscopy has been used to gain detailed information about the effects of atomic configurational changes in the 25-75 percent composition region of the iron-cobalt alloy system. The results indicate that there are competing contributions to the hyperfine interactions and that some of these contributions are dependent on local atomic environment. Also indicated is a spin polarization of the conduction electrons which is positive in sign. In addition, the possibility has been established for using the Mössbauer effect to determine the temperature dependence of the short range order parameter."

Further study of the magnetic structure using polarized neutrons using ordered and disordered alloys should clarify the relationship between atomic configurations and the magnetic electron structure.

Theoretical studies of magnetic ordering using Green's function techniques have been successful in predicting the temperature variation of spin correlations in the paramagnetic region.

Publications:

B. DeMayo, D. W. Forester and S. Spooner, "Effects of Atomic Configurational Charges on Hyperfine Interactions in Concentrated Iron-Cobalt Alloys." (abstract submitted to Magnetism Conference)

B. DeMayo, "A Mössbauer Investigation of Atomic Ordering Effects in the Iron-Cobalt Alloy System." (in preparation)

S. A. Scales and H. A. Gersch, "Green's Function Theory of the Heisenberg Paramagnet." (abstract submitted to Magnetism Conference)

Theses:

B. DeMayo, "A Mössbauer Investigation of Atomic Ordering Effects in the Iron-Cobalt Alloy System." (Physics)

N. C. Koon, "A Mössbauer Effect Investigation of Metamagnetic FeCO_3 ." (Physics)

S. A. Scales, "Green's Function Theory of the Heisenberg Paramagnet." (Physics)

Graduate Students:

Ben DeMayo (Ph.D.)

Sam Scales (Ph.D.)

T.H.B. Sanders (Ph.D.)

N. C. Koon (Ph.D.)

J. W. Lynn (M.S.)

P. S. Keith (M.S.)

7. A New Technique for Detection of Infrared

Radiation - A. L. Stanford

Description of Work Performed:

The pyroelectric effect in biological materials has been pursued in recent months, without much success. Crystalline forms of sodium ribonucleate were the first to be investigated. Various forms of synthetic nucleic acids were prepared in either crystalline or polycrystalline wafer form suitable for pyroelectric detectors. These included adenylic acid, cytidylic acid, and guanylic acid disodium. Powdered forms of thymidylic acid and uridylic acid were pressed into wafers, but contained several percent moisture.

Results:

To date, acceptable forms of nucleic acids for use as pyroelectric detectors have not been found.

Graduate Students:

R. A. Lorey (Ph.D.)

8. The Physical and Functional Aspects of

Integrated-Circuit Technology - K. L. Su

In the circuit phase of the research, work has been done on new methods of realizing the positive-impedance converter and new techniques of network synthesis using the PIC. A new circuit which uses two negative resistances and one controlled source has been found to be capable of realizing the positive-impedance converter. In the synthesis part of the study, effort has been concentrated on the synthesis of driving-point impedances using RC elements and the PIC.

Several circuits have been found to be suitable for this purpose. Comparison of these circuits with those using negative converters indicate definite advantages in using the positive converters. Some preliminary studies have also been done on the sensitivity problem of the networks using positive converters.

In the material and device areas, experimental studies considered both bulk and sputtered-film semiconductors. In the bulk sample studies several of the error reduction techniques were implemented. Also, preliminary measurements with a pulsed E-field supply indicated that mobilities of low resistivity samples (less than one ohm cm) could be obtained without the sample heating associated with D.C. drift field approach.

Electrical measurements were made on two highly oriented Ge films of thickness .35 and 2.1 microns. Sample conductivity, majority carrier type, and minority carrier lifetime were obtained. Although the target material was n-type, both films were p-type with resistivities in the .2 ohm cm range. The thicker film had the lower resistivity and a lifetime approaching the bulk value for Ge. As more samples become available, a correlation should develop between the sputtering conditions and film electrical parameters. Drift mobility measurements were not successful. Unlike the bulk semiconductor surfaces, emitter and collector probes on the films always produced a low resistance, ohmic contact. This is a departure from the normal conditions present in drift mobility experiments on bulk samples. A gold/antimony deposition and diffusion gave good ohmic

contacts for attaching potential leads to the films.

In the semiconductor interface study, activities have been aimed at increasing the understanding of the interface between semiconductor and metals or the oxide. Of particular interest has been the problem of internal photomission which relates to the barrier height at the interface. The method used is to irradiate the sample with the ultra-violet light and measure the photoemitted current for surfaces characterized by reflectivity measurements. The reflectivity experiment has been set up and studies preliminary to the measurements of photoconductive properties are underway. Studies will be extended to surfaces precisely characterized by LEED and Auger Spectroscopy. For these studies a special ultrahigh vacuum apparatus is being constructed and equipped. An auxiliary pumping system for these measurements, including a turbomolecular pump and a forepump, have been ordered under the program.

Paper Submitted for Publication:

N. W. Cox, Jr., and K. L. Su, "Operational-Amplifier Realization of the Nullor and the Universal-Impedance Converter," submitted to the IEEE Journal of Solid-State Circuits.

<u>Students</u>	<u>Department</u>	<u>Level</u>
J. H. Taylor	Physics	Senior
R. S. Gordy	E.E.	M.S.
D. R. Cobb	E.E.	Ph.D.
C. D. Kim	E.E.	Ph.D.
D. W. Covington	E.E.	Ph.D.
F. L. Grismore	E.E.	Ph.D.

9. Collisional De-excitation of Atomic Particles -

E. W. Thomas

Objective of the Research:

The objective of the work is the study of mechanisms whereby light atoms of some keV energy interact with atmospheric gases. In particular, it is intended to study the collisions of excited H and He atoms which result in the stripping of the excited electron. Protons and alpha particles from the sun are responsible for inducing certain types of auroral phenomena. The presence of these fast moving particles may be diagnosed by observing Doppler shifted emission which is produced when the projectiles are neutralized through the process of charge transfer into an excited state. It has been suggested that collisional destruction of the excited atom before it emits a photon may seriously affect the quantitative validity of the diagnosis which is based on such measurements.

The experiments are designed to investigate the process of formation and destruction of excited atoms at projectile energies of 5 to 30 keV. Work will be directed primarily at the metastable states of the neutralized projectiles since this greatly simplifies the problems of detection. Data from this study can be readily extrapolated to higher levels by well established theoretical rules.

The program will determine cross sections for the formation of the metastable state of hydrogen as protons and ground state atoms traverse targets of helium and nitrogen. Measurements will be made as a function of the distance of closest approach between the

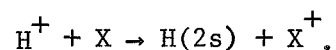
colliding atoms. Also the experiments will be carried out using metastable beams and monitoring their destruction. The cross section for stripping the excited electron into the continuum will be measured directly.

Research Performed in the Current Period:

During the present reporting period there have been two main objectives. The first task was to complete a study of the operational properties of channel electron multipliers, a device which may be used as a particle detector of high gain and low noise. These have been utilized in many space applications, however there has been inadequate study of their operating characteristics. The second objective was to commence detailed study of atomic collision processes.

The study of the channel electron multiplier has been completed and some of the results submitted for publication. As a result of these studies the use of channel electron multipliers has become routine in the work under this grant and also in other atomic collision studies on this campus.

A start has been made on the detailed investigation of atomic collision processes. The apparatus has been finally assembled and careful checking of the operation of each component is being carried out. The apparatus is currently being used to study the reaction:



This is being done as a preliminary to the detailed study of collisional destruction phenomena. There has been some very recent work on this problem in other laboratories and a comparison of data will be useful. The methods that will be used in the final analysis of collisional destruction data require that this cross section be known for all targets that are of interest. The preliminary studies of this problem have involved a helium and nitrogen target. Total cross sections have been estimated and appear to be in general agreement with measurements by other groups. Studies have been made of the angular scattering in the charge transfer process. It is found that the angular distribution of metastably excited atomic hydrogen is different from the distribution for ground state hydrogen. Further refinements of the apparatus are being made in order to confirm this observation.

This program will continue to carry out a brief study of the charge transfer problem with the major objective of proving the operation of the apparatus. Next a gas cell will be placed in the beam preparation region to neutralize part of the projectile flux. Studies will then be made of the mechanisms by which atomic hydrogen is excited in the reaction $H(1s) + X \rightarrow H(2s) + X$ and de-excited in the reaction $H(2s) + X \rightarrow H^+ + e + X$. The target X will be either nitrogen, oxygen or helium. It is expected that some of the studies using neutral beams will be completed during the next six month period.

Papers Submitted for Publication:

A paper entitled "The Relative Detection Efficiency of Funnelled Channel Electron Multipliers for Low Energy Protons and Argon Ions" has been submitted to the Journal of Scientific Instruments for publication.

Graduate Students:

Mr. R. L. Fitzwilson continues to work towards his Ph.D. degree on this project.

10. Microwave Absorption by Gases - T. L. Weatherly

The microwave absorptions studied are associated primarily with changes in molecular rotation energies. However, the absorption frequencies are influenced slightly by nuclear electric quadrupole moments and, in the case of an applied electric field, by the molecular dipole moment (Stark effect). The purpose of these studies is to test the theory for quadrupole interactions in molecules containing two and three identical quadrupolar nuclei and to measure the quadrupole coupling constants and electric dipole moments of such molecules.

The theory for combined Stark effect and nuclear electric quadrupole interaction in molecules containing three identical quadrupolar nuclei was worked out in this laboratory by Dr. C. R. Nave and applied to the molecules PCl_3 and POCl_3 . The results of Dr. Nave's work are summarized in the paper listed in the last report. Dr. P. B. Reinhart applied this theory to the molecules CHCl_3 and CFCl_3 and measured the electric dipole moments of these molecules. Dr. Reinhart

received his Ph.D. in June, 1969, and his work will be reported in a paper which will be written in the near future.

The theory for nuclear quadrupole interaction in molecules containing two identical quadrupole nuclei has been worked out by Mr. W. A. Little. Although there has been previous work on this problem, Mr. Little's treatment is slightly different and is in some ways more complete than the previous treatments. It was originally intended to test this theory on the CH_2Br_2 molecule, and Mr. Foch Tsai has recently measured its spectrum. However, this spectrum contains hundreds of closely-spaced lines, and it has not been possible to identify them. The theory has been extended to include second-order effects which are of particular interest because they offer a means of measuring a component of the electric field gradient tensor which does not appear in the first order theory. It was hoped that inclusion of second order effects might clear up certain small discrepancies in some of our earlier work on the SCl_2 molecule. Additional measurements have been made on the SCl_2 spectrum, and it does appear that earlier discrepancies may be explained by Mr. Little's second order treatment. Mr. Little will use this work as a basis for his Ph.D. dissertation.

The K-band absorption cell mentioned in the last report has been used very successfully to observe the emission of microwaves by ammonia. A great deal of work remains to be done on this problem, and Mr. Foch Tsai will take part in these investigations.

Graduate Students:

P. B. Reinhart - Received his Ph.D. in June 1969.

William A. Little - Candidate for Ph.D.

Foch Tsai - Candidate for Ph.D.

11. Control of Systems with Boundedness Constraints -

R. P. Webb

Account of the Research:

The objective of the research is to develop a procedure for synthesis of a controller for a discrete-time tracking system which will minimize some criterion of cost, subject to additional constraints on the tracking error, the states of the system and the control variables. The optimization procedure is performed using a combination of Lagrange multipliers and a modified form of the Kuhn-Tucker theorem. It has been established that the controller can be synthesized as a matrix of optimal control laws, where each of the control laws corresponds to one of the possible combinations of trajectory points and control inputs constrained to their respective boundaries. The Kuhn-Tucker theorem is used to establish a criterion for selecting the correct control law from the control law matrix.

Graduate Students:

Mr. P. W. Sowa (Ph.D.)

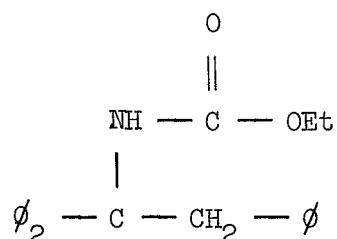
12. Studies in Nitrene Chemistry - L. H. Zalkow

Objectives:

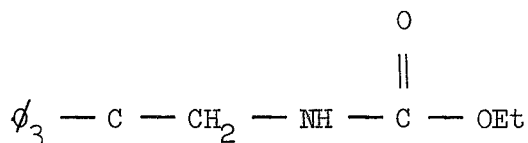
A study of the properties and reactions of nitrenes is proposed. Nitrenes are high energy electron-deficient nitrogen species; the parent compound, NH , has been observed to be a component of the sun, of comets, and of Jupiter; nitrenes have also been postulated as intermediates in a number of organic reactions. This study will include investigation of the electronic structure of nitrenes and investigations of the reactions of nitrenes with organic and inorganic substances. Results of this study should improve our understanding of why these species exist in space, how they may interact with man and spacecraft, and how they may be utilized in space exploration.

Description of Work and Results:

The Electronic Nature of Carbethoxynitrene. The following two products have been isolated from the reaction of carbethoxynitrene with 1,1,1-triphenyl ethane:



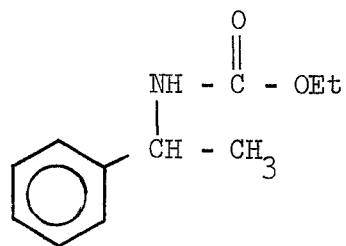
I



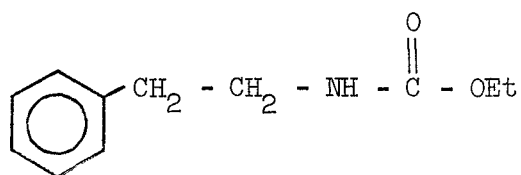
II

These results indicate that both singlet and triplet nitrene attacked the substrate (1,1,1-triphenyl ethane).

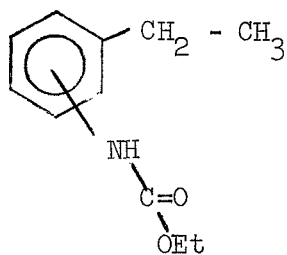
Reaction of carbethoxynitrene with ethyl benzene produced the following products:



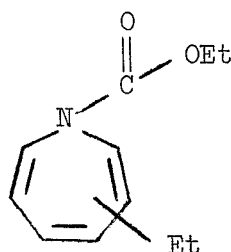
III



IV



V



VI

The ratio of III to IV is an indication of the nucleophilicity of the attacking nitrene. This ratio was found to be much greater than one. The mechanism for the formation of VI may be explained in terms of singlet carbethoxynitrene. Further product analysis is underway.

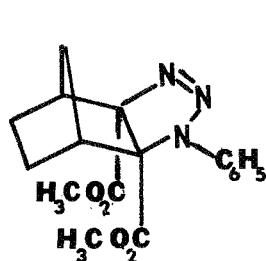
Complexes of Aromatic Azides with Transition Metals.

Attempts have been made to prepare complexes of aromatic azides with cobalt, nickel, and copper compounds. The aromatic azides are stable in the presence of these metal ions and there is evidence from spectral measurements on solutions that complexes are formed with copper (II). No solid complexes have been isolated.

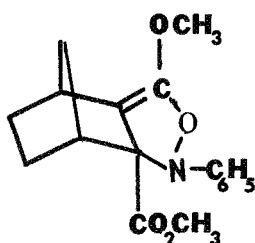
The Reaction of Benzenesulfonyl Azide with Bicyclic Olefins.

A number of bicyclic olefins such as norbornylene and substituted norbornenes have been found to react with various azides under thermal conditions to give exo and endo aziridines via intermediate exo triazolines. The formation of endo aziridines from exo triazolines appears to occur by carbon-carbon bond cleavage to give an intermediate 3-diazomethylcyclopentane-2-carboxaldehydeimine followed by reformation of the carbon-carbon bond with inversion. This intermediate has not as yet been trapped.

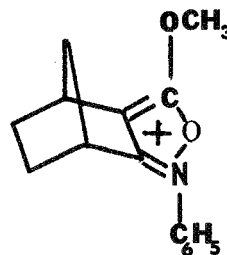
The interesting product II has been produced on pyrolysis of I and it gives the stable ion III as the base peak in its mass spectrum.



I



II



III

The various azides investigated (aryl and benzenesulfonyl) on photolysis give nitrenes which predominantly add to the double bonds of the bicyclic olefins but give a small amount of C-H insertion products.

Conclusions:

In the case of carbethoxynitrene, both the singlet and the triplet nitrene react with the organic substrate.

In the reaction of benzenesulfonyl azide with bicyclic alkenes, the thermal reaction does not involve a nitrene while the photolytic reaction does involve a nitrene. The stereo-chemistry of attack of the nitrene is almost exclusively exo. A number of new and novel compounds have been isolated upon pyrolysis of bicyclic triazolines and mass spectral studies of the fragmentation patterns of these substances are under investigation.

Publications:

"The Reaction of Benzenesulfonyl Azide with cis-endo and cis-exo-Norbornene-5,6-dicarboxylic Acid Anhydrides and Methyl Esters,"
R. L. Hale and L. H. Zalkow, Tetrahedron, 25, 1393 (1969).

Graduate Students:

R. H. Hill	Ph.D.
C. Shen	Ph.D.
C. Kirkwood	Ph.D.

III. CONCLUSIONS

The NASA Multidisciplinary Grant NGL 11-002-018 continues to stimulate research on the campus and its effectiveness is demonstrated by the number of publications (3), submissions (8) and presentations (1) during the six month period, March 15, 1969 to September 14, 1969.

Through the grant graduate students are engaged in quality research activities and students in the following categories received financial support from the grant: Undergraduates - 2, M.S. - 5, Ph.D. - 18, and Post Doctorals - 2.